of this change is an increase in the C(2)C(3)H bond angle, resulting in the 3,3′-H's moving apart even though the inter-ring bond is shortened. The shift of the 1318-cm^{-1} mode to higher energy and the enhancement of the δ(CCH) would then be expected. In addition, the shift of the mode at 1171 cm^{-1} with reduction can be understood if the mode contains substantial contribution from the 3,3′-H's, since the steric crowding of these H's would be reduced considerably as they move apart. Indeed, additional modes observed at 1215, 1230, and 1280 cm^{-1} might also be attributed to the other C–C–H deformations of the reduced bipyridine.

Conclusion

The appearance of two sets of A_1 vibrations for the singly reduced species in the RR spectrum and the stepwise reduction of the intensity of the $\pi \rightarrow \pi^*$ transition in the UV spectrum clearly support a single-bpy-localized model for the redox electron. Both the RR and FTIR spectra for the reduced species indicate that there is interaction between the bpy-localized redox orbital and an empty metal d orbital. This interaction results in stronger π back-bonding between the cyanides and the metal and a subsequent decrease in C≡N bond order for the cyanides. The enhancement of ν(Ru—CN) and ν(C≡N) when the MLCT of the unreduced species is probed has been interpreted as an elongation of the Ru—C bond and a compression of the C≡N bond as electron density is removed from the filled d orbitals and back-bonding decreases. Thus, the bond length changes in the Ru—C≡N portion of $Ru(bpy)_2(CN)_2$ are different upon reduction and excitation into the ^{1}MLCT state. Also, a decrease in the inter-ring separation and an increase in the separation between the 3- and 3′-hydrogens in the photoexcited and redox states are suggested to account for the observed resonance enhancement and the frequency shifts of CCH deformations and inter-ring stretch. The RR data also indicate that the average frequency shift of bipyridine modes upon reduction may be on the order of 10 cm^{-1}.

Acknowledgment. We thank Dr. Franco Scandola for portions of the $Ru(bpy)_2(CN)_2$ used in this research and Dr. Anton Schreiner for the use of his argon ion laser. We also thank Drs. Robert Donohoe and C. Drew Tait for their helpful comments. This work was partially supported by NSF Grant CHE-85-07901.

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Electron-Transfer Autocatalytic Formation, Intramolecular Charge Transfer, and Qualitatively Different Solvatochromism of σ and π Transition-Metal Carbonyl Complexes with Polynitrile Ligands[†]

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Received December 12, 1988

Mononuclear transition-metal carbonyl complexes (η^1-TCNE)$Cr(CO)_2(C_6Me_6)$ and (η^1-L)$Mn(CO)_2(\eta^5\text{-}C_5Me_nH_{5-n})$ with σ (end-on) coordinated ligands L = tetracyanoethene (TCNE), 2,5-dimethyl-7,8-dicyano-*p*-quinone diimine, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and the complexes (η^2-TCNE or $\eta^{\geq 2}$-TCNQ)$M(CO)_5$ (M = Cr, W) and (η^2-fumarodinitrile)$Mn(CO)_2(\eta^5\text{-}C_5Me_5)$ with a π (side-on) coordinated polycyano ligand have been studied by cyclic voltammetry (TCNE complexes) and electron absorption spectroscopy. Reduction potentials of the complexes were found above and below the values of free TCNE, indicating varying degrees of metal-to-ligand electron transfer in the ground state. This electron transfer is confirmed by vibrational spectroscopy and UV/vis/near-IR spectral response on C_5R_5 ligand modification. Solvent-induced dissociation into the simultaneously ESR detectable paramagnetic metal fragment and the anion radical of the ligand was observed in one instance. Intense charge-transfer (MLCT/LMCT) transitions of the complexes occur in the visible and near-infrared part of the spectrum. The π-coordinated complexes were found to exhibit a very different spectral response toward solvent variation than the σ-bonded derivatives.

Introduction

There is increasing recognition of the essential role of electron-transfer processes in organometallic chemistry and in areas (catalysis, organic synthesis) that make use of organometallics.[1–5] The tetracyanoethene (TCNE) molecule may safely be called the *E. coli* of electron-transfer chemistry in view of the numerous investigations using this highly π-electron-deficient system as a potential one-electron acceptor.[1,5,6] While even the reactions of TCNE with main-group organometallics,[2] e.g. organosilicon compounds, reveal an enormous variability,[6] the number of reviews[1,6,8] and recent solid-state studies of transition-metal complexes with π-accepting TCNE[9] and the related tetracyano-*p*-quinodimethane (TCNQ)[10] indicate that this seems to be a particularly fruitful area of organometallic chemistry.[6,11] Much effort has been devoted to the structural aspect of bonding; these acceptor ligands may coordinate in a σ fashion (via the nitrile N lone pair)[10c,12–14] or in a π type of arrangement (i.e. via the C═C olefinic bond in TCNE)[8,15] or stay "free" as in complexes with certain coordinatively saturated metallocenes.[9,16]

Besides the structural ambivalence, there is also frequent ambiguity concerning the oxidation states within these complexes.

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[†] Part 5 of a series on electron-transfer-catalyzed substitution in carbonyl complexes. Part 4: Reference 25.

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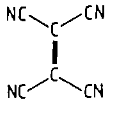
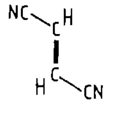
Chart I

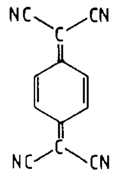
1: (h^1-TCNE)Mn(CO)$_2$(h^5-C$_5$Me$_5$)
2: (h^2-DCNE)Mn(CO)$_2$(h^5-C$_5$Me$_5$)
3: (h^1-2,5-DM-DCNQI)Mn(CO)$_2$(h^5-C$_5$Me$_5$)
4: (h^1-TCNQ)Mn(CO)$_2$(h^5-C$_5$Me$_5$)
5: (h^1-TCNE)Mn(CO)$_2$(h^5-C$_5$H$_4$Me)
6: (h^1-TCNE)Cr(CO)$_2$(h^6-C$_6$Me$_6$)
7: (h^2-TCNE)Cr(CO)$_5$
8: (h^2-TCNE)W(CO)$_5$
9: (h$^{\geq 2}$-TCNQ)Cr(CC)$_5$
10: (h$^{\geq 2}$-TCNQ)W(CO)$_5$



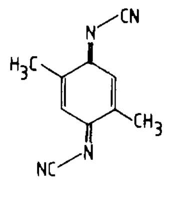
TCNE



DCNE



TCNQ



2,5-DM-DCNQI

Since TCNE and TCNQ are reduced very easily to anion radicals, to dianions, and even radical trianions,[17] an establishment of the correct oxidation state often requires structural information from X-ray diffraction or vibrational spectroscopy.[9,12,14] Of particular interest are those complexes in which metal and ligand oxidation states are not well defined and which exhibit some degree of covalent bonding.[18] Sulfur complexes of this kind with iron[19] and copper centers[20] play an important role in biochemistry due to their excellent electron-transfer properties; we have recently reported a similar situation in the case of paramagnetic manganese carbonyl complexes of nitrogen heterocycles.[21]

While ESR spectroscopy can provide detailed information on such problems (formulation A or B in eq 1) in the case of paramagnetic ($S = {}^1/_2$) species,[20,21] the assessment of contributions from A or B in eq 1 to the electronic structure of an even-electron system may be much more difficult.[22]

$$\underset{\text{A}}{\text{R}_n\text{ML}} \leftrightarrow \underset{\text{B}}{[(\text{R}_n\text{M}^{\bullet+})(\text{L}^{\bullet-})]} \leftrightarrow \underset{\text{C}}{[(\text{R}_n\text{M}^{2+})(\text{L}^{2-})]} \qquad (1)$$

In this paper, we describe the use of electrochemical and IR and UV/vis/near-IR spectroscopic criteria in order to adequately describe the bonding in σ- and π-coordinated transition-metal carbonyl complexes (Chart I) of TCNE, TCNQ, and two related ligands.

The TCNE (**1**, **5–8**)[14,23-25] and TCNQ complexes (**4**, **9**, **10**)[14,25] have been referred to in previous communications. Due to their lability, these compounds were not always adequately characterized; only recently did we correct earlier claims of a π coordination[23] in manganese complexes such as **1** and **5**.[14,25] Detailed IR vibrational studies[25] revealed σ (η^1, N) coordination in TCNE and TCNQ complexes (**1**, **4–6**) of the mixed carbonyl/carbocycle metal fragments whereas the complexes **7–10** contain π ($\eta^{\geq 2}$, C=C) coordinated pentacarbonylmetal fragments. The exact structure of (TCNQ)M(CO)$_5$ complexes, i.e. π coordination to the exocyclic double bond(s) or to the π system of the six-membered ring, could not be unambiguously established in the absence of a crystal structure determination; IR data suggest a rather symmetrical arrangement.[25] The ligands 1,2-(*E*)-dicyanoethene (DCNE = fumarodinitrile)[13a,26] and 2,5-dimethyl-7,8-dicyano-*p*-quinone diimine (2,5-DM-DCNQI)[27] were employed because of their relation to TCNE and TCNQ; solids that conduct extremely well and contain partly reduced 2,5-DM-DCNQI were recently obtained with Cu$^+$ as cation.[27a,b] We shall show in this work that infrared vibrational data and solvatochromic behavior suggest η^1 (N) coordination in **3** but η^2 (C=C) attachment in **2**.

It turned out in the course of this work that the very long wavelength charge-transfer absorption bands are not only interesting with regard to their assignment as predominantly metal-to-ligand (MLCT) or ligand-to-metal charge transfer (LMCT);[28] variation of the solvent has exhibited some band structuring and an initially puzzling solvatochromic response. While conventional solvent scales (E_T[29] or E^*_{MLCT}[30a]) derived for[30a] and applied to numerous σ-bonded carbonylmetal complexes[30,31] could be suc-

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cessfully used for the σ-bonded TCNE systems, the π complexes with $M(CO)_5$ fragments exhibit a completely different response, as will be outlined in this paper. A detailed study of solvatochromism seems to be warranted, since it is recognized now that the role of the intervening medium is most essential for the effectiveness of electron transfer;[32] the hydrophobic environment in which organometallic chemistry is usually carried out should very much favor such interactions.

Experimental Section

Instrumentation: ESR, Varian E9, X band (9.5 GHz); IR, Jasco A100; UV/vis/near-IR, Shimadzu UV160, Perkin-Elmer Lambda 9; cyclic voltammetry, PAR 363 potentiostat, Bank VSG 72 ramp generator, glassy-carbon working electrode, saturated calomel reference electrode (SCE), 0.1 M solutions of tetrabutylammonium perchlorate in acetonitrile as electrolyte. All measurements were done under an argon atmosphere in subdued light; the rapid dissociation of many complexes in polar solvents required the dissolution of solid materials in dry, spectrograde solvents immediately before the measurements.

Syntheses of the compounds **1** and **4–10** have been described before.[14,24,25] Compounds **2** and **3** were prepared by reacting photogenerated $(THF)Mn(CO)_2(C_5Me_5)$[33,34] in THF solution with 1 equiv of the dicyano ligand. The solutions either immediately turned blue (2,5-DM-DCNQI) or changed to blue after 5–10 min of reaction time (DCNE). Since even low-temperature (−40 °C) column chromatography on Florisil led to much decomposition, both dark blue complexes were isolated by evaporation of the solvent. In contrast to the case for **1**, **7**, or **8**[25] these two compounds were too labile for conventional elemental analyses due to their pronounced air and light sensitivity.[34] IR (THF): ν_{CN} 2175 (DCNE complex), 2125, 2100 cm^{-1} (2,5-DM-DCNQI complex); for ν_{CO} see Table I; ν_{CC} 1440 (broad, DCNE complex), 1580, 1510, 1460 cm^{-1} (2,5-DM-DCNQI complex).

Results

Reactivity and Structure. Previous studies of the TCNE compounds **1** and **5–8** and the TCNQ complexes **4**, **9**, and **10** have shown that these complexes are formed very rapidly from the free acceptor ligands and solvent or phosphite precursors of the organometallic fragments.[14,24,25] Formation of the 2,5-DM-DCNQI complex is similarly rapid, whereas the reaction with the far less reducible (Table II) DCNE ligand[35] takes about 5–10 min to go from the red precursor $(THF)Mn(CO)_2(C_5Me_5)$[33,34] to the blue mononuclear complex. This vastly accelerated substitution by strong acceptor ligands is a consequence of considerable electron transfer in the ground state, giving rise to an "electron-transfer autocatalytic" process (eq 2–4),[25,26] which involves substitutionally labile 17-electron species.[3-5,37]

start

$$(\pi\text{-CN}_x) + R_nML \rightleftharpoons (\pi\text{-CN}_x)^{\bullet-} + \underset{17e}{(R_nML)^{\bullet+}} \quad (2)$$

propagation

$$(R_nML)^{\bullet+} + (\pi\text{-CN}_x) \rightarrow [R_nM(\pi\text{-CN}_x)]^{\bullet+} + L \quad (3)$$

$$[R_nM(\pi\text{-CN}_x)]^{\bullet+} + R_nML \rightarrow \underset{\text{product}}{R_nM(\pi\text{-CN}_x)} + (R_nML)^{\bullet+} \quad (4)$$

Not only have highly resolved vibrational spectra been extremely valuable in determining the symmetry, conformational isomerism, and coordination status of the TCNE and TCNQ compounds,[25] significant low-energy (acceptor ligand: $\nu_{C=C}$, $\nu_{C\equiv N}$)[9,12-14,17] and high-energy shifts (metal fragment: $\nu_{C\equiv O}$, Table I)[21,34] also indicate considerable intramolecular electron transfer in the products according to formulation B in eq 1.[12]

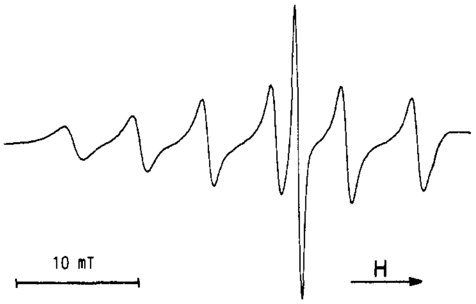

Figure 1. ESR spectrum of partially dissociated **4** at 300 K in THF solution, showing TCNQ$^{\bullet-}$ (g = 2.003) and a sextet from a low-spin manganese(II) species[21b] (g = 2.031; $a(^{55}Mn)$ = 5.5 mT).

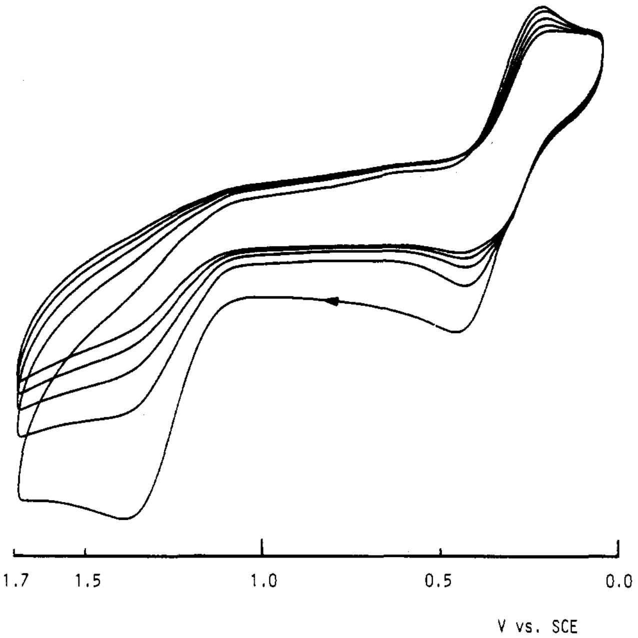

Figure 2. Cyclic voltammogram of complex **8** in acetonitrile/0.1 M Bu_4NClO_4, showing reversible reduction and irreversible oxidation.

The 2,5-DM-DCNQI and TCNQ complexes **3**, **4**, **9**, and **10** are more labile than their TCNE analogues; the negative charge of the (partially) reduced form that is responsible for the bonding to the oxidized metal fragment is distributed over more π centers in those systems.[38] Unexpectedly, the complex **2** also proved to be quite labile; we shall show later that vibrational and solvatochromism data suggest a π (C=C) coordination in **2** in contrast to the σ (N) coordination of the polycyanoolefin ligands in **1**,[25] **3**, and **4**.[25] The lability of the mononuclear DCNE, 2,5-DM-DCNQI, and TCNQ complexes has precluded electrochemical studies and some spectroscopic investigations in coordinating (donor) solvents; one consequence of this solvent-induced dissociation is the formation in THF or acetonitrile solution of both paramagnetic ($S = {}^1/_2$) species[21,38] from **4** (eq 5, where CIP denotes the contact ion pair and SSIP denotes the solvent-separated ion pair), observed as a solvent-separated radical-ion pair[2,3c] by ESR spectroscopy (Figure 1).

$$[M^+L^{\bullet-}] \rightarrow \underset{\text{CIP}}{M^+\text{---}L^-} \xrightarrow{\text{solvent}} \underset{\text{SSIP}}{M^+(\text{solv}) + L^{\bullet-}(\text{solv})} \quad (5)$$

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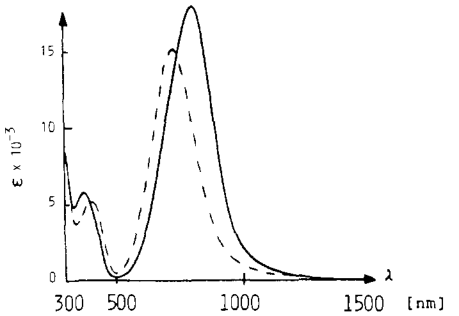

Figure 3. Absorption spectra of complex **1** in toluene (—) and acetonitrile solution (- - -).

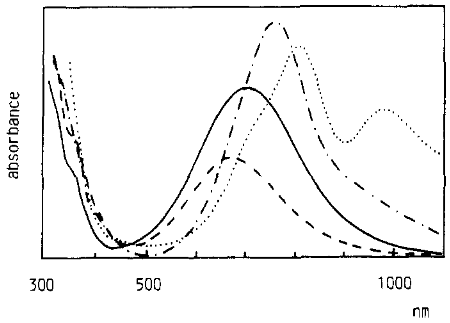

Figure 4. Absorption spectra of complex **8** in acetonitrile (—), THF (- - -), benzene (-·-), and cyclohexane solution (···).

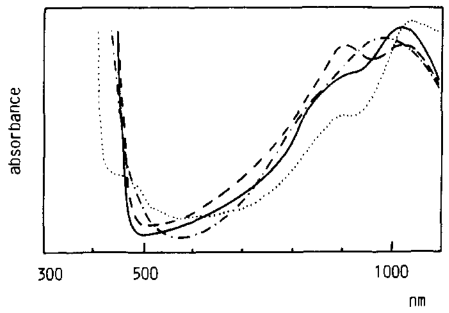

Figure 5. Absorption spectra of complex **10** in acetonitrile (—), acetone (- - -), benzene (-·-), and cyclohexane solution (···).

Cyclic Voltammetry. The TCNE complexes **1** and **5**–**8** could be reversibly reduced in cyclic voltammetry experiments at potentials around 0 V vs SCE. An ESR spectrum of reduced **8** showed evidence for a change to a σ-coordinated anion radical complex (cf. formulation A in eq 7);[25] rapid relaxation corresponding to strong contributions from resonance form B in eq 7 is thought to be responsible for the absence of detectable room-temperature ESR signals of the other electrochemically generated anion radicals. Oxidation of the complexes in coordinating electrolytes is always irreversible[34,41] (Figure 2) at potentials that do, however, support the electron-transfer autocatalytic mechanism (eq 2–4); the potentials are summarized together with those of all acceptor ligands in Table II.

Electronic Spectroscopy. Complexes **1**–**10** all exhibit intense charge-transfer bands in the red or near-infrared (near-IR) region of the spectrum; the σ complexes **1**, **5**, and **6** and the TCNQ π complexes **9** and **10** show an additional band in the high-energy part of the visible region (Figures 3–5). Most complexes, especially **8**–**10**, reveal a distinct structure of the long-wavelength CT band system in nonpolar solvents (Figures 4 and 5). Similar effects were noted previously for other complexes of the (d^6) organometallic fragments employed here and were attributed to differently polarized transitions involving the three occupied d levels in a low-spin d^6 situation.[30b–d,34,40] Table III summarizes the data obtained in different solvents, Figures 6 and 7 show correlations[31] between energies at the transition maximum and the solvent parameter E^*_{MLCT},[30a] and Table IV contains the parameters A and B of linear equations (eq 6)[30a,b] for some of the

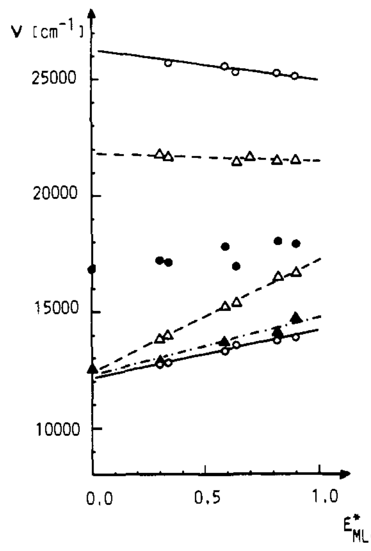

Figure 6. Dependence of absorption maxima of complexes on the solvent "polarity" parameter E^*_{MLCT} (data from Table III): (○) **1**; (●) **2**; (▲) **3**; (△) **6**. Linear correlations from the coefficients from Table IV are shown for the σ-coordinated systems **1** (—), **3** (-·-), and **6** (- - -).

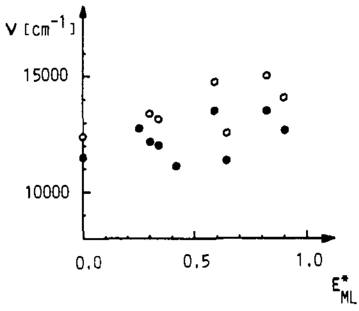

Figure 7. "Correlation" between the absorption maxima of TCNE π complexes **7** (●) and **8** (○) and the E^*_{MLCT} parameters.

$$\nu_{\mathrm{CT}} = A + BE^*_{\mathrm{MLCT}} \qquad (6)$$

complexes studied. The parameter E^*_{MLCT} was derived by Lees and Manuta for complexes (bpy)M(CO)$_4$ (M = Cr, Mo, W)[30a] and has been successfully applied for a number of σ (N) coordinated metal carbonyl complexes.[30,31]

Discussion

Electron-Transfer Autocatalysis, Electrochemistry, and Vibrational Spectroscopy. TCNE, TCNQ, and 2,5-DM-DCNQI[27c] are reduced at such positive potentials (Table II) that electron transfer from electron-rich organometallic systems in the ground state is clearly feasible. The precursors Mn(CO)$_2$(C$_5$Me$_n$H$_{5-n}$)(THF)[37] and Cr(CO)$_2$(C$_6$Me$_6$)(P(OMe)$_3$)[24] have oxidation peak potentials *below* E_{red} of TCNE or TCNQ so that even simple outer-sphere electron transfer can occur.[1,3] M(CO)$_5$(THF) solvates (M = Cr, W) are less easily oxidized;[42] nevertheless, the relatively rapid substitution resulting in complete conversion after a few seconds[25] also suggests greatly accelerated solvent substitution following some initial *chemical* electron transfer (eq 2) in the ground state,[12c,15e] which generates the substitutionally labile (eq 3) 17-electron intermediate $(\mathrm{R}_n\mathrm{ML})^{\bullet+}$.[3,4,37] The catalytic cycle is completed because the radical cation of the product can oxidize the precursor, the solvent[37] or phosphite complex,[24] in another

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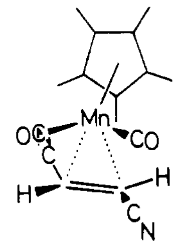
(41) For decomposition pathways cf.: Zoski, C. G.; Sweigart, D. A.; Stone, N. J.; Rieger, P. H.; Mocellin, E.; Mann, T. F.; Mann, D. R.; Gosser, D. K.; Doeff, M. M.; Bond, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 2109.

(42) E_{ox}[M(CO)$_5$(THF)] (M = Cr) is estimated to be 0.6 V vs SCE by using published series[37] and the ligand additivity concept: Chatt, J.; Kan, C. T.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2032.

Chart II



homogeneous electron-transfer step (eq 4). DCNE, on the other hand, is reduced at a much more negative potential than TCNE (1.7-V difference, Table II)[35] and does not exhibit an unusually fast substitution of coordinated THF in (THF)Mn(CO)$_2$(η^5-C$_5$Me$_5$).[34]

As concerns the extent of intracomplex electron transfer (eq 1), the comparison of carbonyl stretching frequencies ν_{CO} in complexes (π-CN$_x$)Mn(CO)$_2$(C$_5$Me$_5$) (Table I) gives a first indication. With increasing reduction potential of the polycyano ligand (Table II) the values for ν_{CO} (A$_1$, B$_1$) become higher and less separated ($\Delta\nu$, Table I). The high-energy shift alone indicates electron flow from the metal fragment to the nitrile ligand, resulting in weaker M → CO back-donation as was shown before for related neutral Mn(I)[34] and Mn(II) compounds.[21] The diminishing spread of the two carbonyl stretching bands as one goes from DCNE via 2,5-DM-DCNQI to the TCNQ and TCNE ligands reflects a decreasing interaction constant k_i and thus stronger π bonding[43] between the metal fragment and the polycyano ligand. This π bonding can occur in a σ or in a π fashion;[25] vibrational spectroscopic studies have indicated nitrile (σ) coordination for **1** and **4–6** and side-on (π) coordination for **7–10**.[25] While the occurrence of two nitrile bands for **3** as well as the solvatochromism (cf. below) suggest bonding via the nitrile N lone pair of the 2,5-DM-DCNQI ligand, we believe that complex **2** contains a π-coordinated fumarodinitrile ligand[44] because of only one nitrile stretching band and because of distinctly different solvatochromic behavior (Figure 6). Herberhold and Brabetz have suggested σ coordination for the related (DCNE)Mn(CO)$_2$(C$_5$H$_5$) on the basis of two olefinic resonances in the ^{1}H NMR spectrum;[26] however, a π-bonded Mn(CO)$_2$Cp fragment would also cause inequivalency of the DCNE protons because π overlap requires a fixed conformation for a π complex[25] (Chart II) as well as for σ complexes.[21] On the other hand, it cannot be ruled out that the change from C$_5$H$_5$ to C$_5$Me$_5$ alone may have some effect or that these systems can show σ *and* π coordination; unfortunately, the dissociative lability of **2** has precluded a ^{1}H NMR study.

Coordination of an electrophilic (organo)metal fragment to a reducible ligand usually causes an increase in the reduction potential of that ligand because of polarization by the electrophile,[34,45] an effect which should not depend on the coordination mode. Metal-to-ligand electron transfer (back-donation) in the ground state may reduce[46] and even reverse this effect, as shown in the series of TCNE complexes (Table II); after exchange of considerable electron density (A → B in eq 1) it may not be the ligand but either the ligand anion or the oxidized metal center that gets reduced (to compounds A and B in eq 7) at rather negative potentials.

$$\begin{tikzcd} & (R_nM^{\bullet+})(L^{\bullet-}) \arrow[d, shift left, "+e^-"] & \\ (R_nM)(L^{\bullet-}) \arrow[rr, leftrightarrow] & {} \arrow[u, shift left, "-e^-"] & (R_nM^{\bullet+})(L^{2-}) \\ \text{A} & & \text{B} \end{tikzcd} \qquad (7)$$

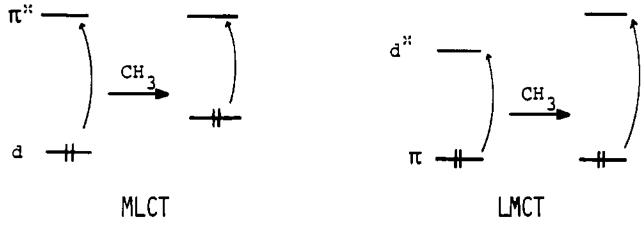


Figure 8. Effect of methyl substitution (R: H → CH$_3$) at the cyclopentadienide ligand for the different kinds of Mn/L charge-transfer transitions in complexes (L)Mn(CO)$_2$(C$_5$R$_5$).

Chart III

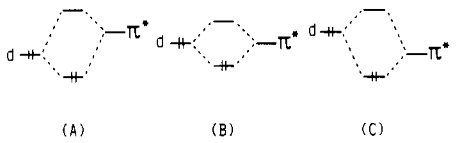
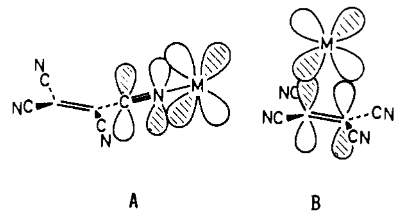


Chart IV



In agreement with the oxidation potentials of the metal precursors[24,37,42] the reduction potentials of the TCNE complexes decrease in the order W(CO)$_5$ > Cr(CO)$_5$ (≈free ligand) > Mn(CO)$_2$(C$_5$Me$_5$) > Cr(CO)$_2$(C$_6$Me$_6$) of the metal fragments. While the W(CO)$_5$ complex does still exhibit "conventional" behavior, including the formation of a (σ-coordinated) anion radical complex (A in eq 7),[25,45] the mixed carbonyl/carbocycle containing metal fragments clearly show the effect of electron exchange in the ground state. Accordingly, the absence of an ESR-detectable signal at room temperature for $\mathbf{1}^{\bullet-}$ or $\mathbf{6}^{\bullet-}$ suggests strong contributions from B in eq 7; the spin residing predominantly at the metal should lead to fast relaxation.[47] The two chromium systems **6** and **7** nicely illustrate the effect of replacement of three strongly π-accepting CO groups by one essentially electron-donating hexamethylbenzene ligand.

UV/Vis/Near-IR Spectroscopy and Solvatochromism. The ambiguity (eq 1) concerning the electronic structure of the compounds discussed in this paper is illustrated by MO interaction diagrams (Chart III).

Symmetry-allowed transitions between the frontier orbitals (Chart IV) may be of the MLCT (A in Chart III) or LMCT type (C in Chart III) or may, in an intermediate situation (B in Chart III), occur between orbitals of considerable metal/ligand mixed character. Complexes **1–10** all exhibit intense ($\epsilon \approx 10^4$ M^{-1} cm^{-1}, Table III) charge-transfer absorption bands in the red to near-infrared part of the spectrum (Figures 3–5). **1**, **5**, and **6** and the TCNQ π complexes **9** and **10** are distinguished by a second intense feature at higher energies of the visible region (Figures 3 and 5).

Chart III can be used to determine whether a transition may be designated as MLCT or LMCT.[28b,48] Increasing methyl substitution at the cyclopentadienide coligand should primarily raise the energy of the interacting metal d orbital.[34] In the case of situation A in Chart III, such a modification should result in a *bathochromic* shift of the charge-transfer band (Figure 8), as

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[43] Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. Cf. similar effects for tetracarbonylmetal complexes: Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68.

[44] Muir, K. W.; Ibers, J. A. *J. Organomet. Chem.* **1969**, *18*, 175.

[45] Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

[46] Ernst, S.; Kohlmann, S.; Kaim, W. *J. Organomet. Chem.* **1988**, *354*, 177.

[47] (a) Bencini, A.; Gatteschi, D. In *Transition Metal Chemistry*; Nelson, G. A., Figgis, B. N., Eds.; Marcel Dekker: New York, 1982; Vol. 8, p 1. (b) For an example cf.: Kaim, W.; Kasack, V.; Binder, H.; Roth, E.; Jordanov, J. *Angew. Chem.* **1988**, *100*, 1229; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1174.

[48] Cf. the argument in: Haga, M.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447. Kaim, W.; Ernst, S.; Kohlmann, S. *Chem. Unserer Zeit* **1987**, *21*, 50.

Table I. Carbonyl Infrared Stretching Frequencies ν_{CO} of the Neutral Complexes (L)Mn(CO)$_2$(η^5-C$_5$Me$_5$) in THF Solution

L	complex	ν_{CO}, cm^{-1}	$\Delta\nu$, cm^{-1}
TCNE	**1**	1985, 1950	35
TCNQ	**4**	1970, 1935	35
2,5-DM-DCNQI	**3**	1970, 1915	55
DCNE	**2**	1905, 1830	75
pz[a]		1918, 1852	66
4-tam[b]		1940, 1880	60

[a] pz = pyrazine.[34] [b] 4-tam = 4-tolylamide.[21c]

Table II. Redox Potentials of Ligands and of TCNE Complexes[a]

compd	$E^{p,a}_{ox}$	$E_{red}(0/1-)$	$E_{red}(1-/2-)$
TCNE		+0.24	−0.77
TCNQ		+0.22	−0.37
2,5-DM-DCNQI		+0.05	
DCNE		−1.36	
(TCNE)Mn(CO)$_2$(C$_5$Me$_5$) (**1**)	+0.96	−0.14	*b*
(TCNE)Cr(CO)$_2$(C$_6$Me$_6$) (**6**)	+0.84	−0.45	*b*
(TCNE)Cr(CO)$_5$ (**7**)	+1.19	+0.26	*b*
(TCNE)W(CO)$_5$ (**8**)	+1.37	+0.32	*b*

[a] In acetonitrile/0.1 M Bu$_4$NClO$_4$; potentials in V vs SCE. Anodic peak potentials are given for irreversible oxidation processes; scan rate 100 mV/s. [b] Irreversible second reduction.

Table III. Solvent Parameters and Solvatochromism Data for Complexes

solvent param [ref]	isooctane, *n*-hexane (cyclohexane)	mesitylene	toluene	benzene	CHCl$_3$	THF	DCE	benzo-nitrile	nitro-benzene	acetone	aceto-nitrile
E*$_{MLCT}$ [30a]	0.00	0.25	0.30	0.34	0.42	0.59	0.64			0.82	0.98[g]
E_T [29]	30.9 (31.2)		33.9	34.5	39.1	37.4	41.9	42.0		42.2	46.0
DN [53]	0.0			0.1	~0.0	20.0	0.0	11.9	4.4	17.0	14.1

	ν, cm^{-1}										
complex	isooctane *n*-hexane (cyclohexane)	mesitylene	toluene	benzene	CHCl$_3$	THF	DCE	benzo-nitrile	nitro-benzene	acetone	aceto-nitrile
(C$_5$Me$_5$)(CO)$_2$Mn(TCNE) (**1**)	insol		12 670[a]	12 780		13 280	13 470			13 710	13 850
			26 400[b]	25 700		25 510	25 250			25 252	25 125
(C$_5$Me$_5$)(CO)$_2$Mn(DCNE) (**2**)	16 800	17 120	17 150		17 790	17 000				17 950	17 850
(C$_5$Me$_5$)(CO)$_2$Mn(DDCNQI) (**3**)	12 460		12 730			13 660				14 060	14 770
	9 000 sh		10 500 sh			10 500 sh					
(C$_5$Me$_5$)(CO)$_2$Mn(TCNQ) (**4**)			9 510								
(C$_5$MeH$_4$)(CO)$_2$Mn(TCNE) (**5**)			12 150								
(C$_6$Me$_6$)(CO)$_2$Cr(TCNE) (**6**)	insol		13 770	13 980		15 120	15 290			16 420	16 520
			21 740	21 640		21 600	21 370			21 460	21 460
(CO)$_5$Cr(TCNE) (**7**)	(11 400)	12 720[e]	12 160[c]	12 010	11 100[e]	13 490	11 320	12 040	11 830[e]	13 510	12 700
(CO)$_5$W(TCNE) (**8**)	(12 390)		13 380[d]	13 140		14 770	12 530	13 440		15 060	14 080
	(10 190)		11 000 sh				10 500 sh				
(CO)$_5$Cr(TCNQ)[f] (**9**)	<9 090		9 360	9 380		9 770	<9 090	<9 090		9 970	10 040
			11 200 sh	11 200 sh		11 000 sh				11 200 sh	11 400 sh
(CO)$_5$W(TCNQ)[f] (**10**)	9 580		10 360	10 160		9 610	10 020			9 790	9 810
	11 000 sh		12 000 sh	12 000 sh		10 950				11 070	11 110 sh

[a] ϵ = 17 000 M^{-1} cm^{-1}. [b] ϵ = 5400 M^{-1} cm^{-1}. [c] ϵ = 7400 M^{-1} cm^{-1}. [d] ϵ = 7000 M^{-1} cm^{-1}. [e] From ref 23b. [f] Shoulders between 11 000 and 12 000 cm^{-1} due to IL transitions of TCNQ$^{\bullet-}$. [g] Better correlations were found with E^*_{MLCT}(acetonitrile) = 0.90.[31b]

Table IV. Parameters of the Equation $\nu_{MLCT} = A + BE^*_{MLCT}$

complex	A, cm^{-1}	B, cm^{-1}	r^a
(TCNE)Mn(CO)$_2$(C$_5$Me$_5$) (**1**)	12 114	1969	0.995
	27 268	−2605	0.914
(DCNE)Mn(CO)$_2$(C$_5$Me$_5$) (**2**)	16 758	1212	0.822
(2,5-DM-DCNQI)Mn(CO)$_2$(C$_5$Me$_5$) (**3**)	12 253	2457	0.965
(TCNE)Cr(CO)$_2$(C$_6$Me$_6$) (**6**)	12 339	4752	0.996
	21 816	−453	0.802
(TCNE)Cr(CO)$_5$ (**7**)	11 554	1073	0.321
(TCNE)W(CO)$_5$ (**8**)	12 488	2208	0.669
(TCNQ)W(CO)$_5$ (**10**)	9 775	1398	0.699

[a] Correlation coefficient.

has been demonstrated for mono- and binuclear complexes of pyrazine.[34] The same result is observed here for the DCNE complexes; we find ν_{CT} = 18 400 cm^{-1} for **2** in ethanol, while Herberhold and Brabetz report 19 500 cm^{-1} for (DCNE)Mn(CO)$_2$(C$_5$H$_5$) in the same solvent.[26] In an LMCT situation (formulation C in Chart III) *after* the preceding ground-state metal-to-ligand electron exchange, the replacement of H by CH$_3$ in the cyclopentadienide should *increase* the transition energy according to Figure 8. Such an effect, however small, is indeed observed for the couple **5**/**1** (Table III), supporting the conclusions drawn from electrochemistry and vibrational spectroscopy. A situation corresponding to formulation B in Chart III has been found in odd-electron complexes of *p*-phenylenediamides(1−) with Mn(CO)$_2$(C$_5$R$_5$) fragments;[21] the weak spectral response toward a change of R and solvent is in agreement with the ESR spectroscopically determined balanced spin distribution between the metal fragment and the noninnocent ligand.[21]

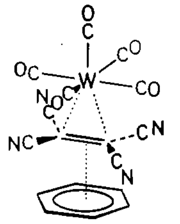
The absolute transition energy should be smallest in a situation corresponding to formulation B in Chart III, provided that the metal/ligand interaction does not change. In the series of manganese systems studied in toluene (Table III), the TCNQ complex **4** exhibits the lowest absorption energy. The higher value for the TCNE analogue **1** is attributable to a stronger metal/ligand interaction: being reduced at the same potential as TCNQ (Table II), TCNE provides more π^* electron density at the coordinating center in this smaller ligand.[38,49] In agreement with the more negative reduction potentials and thus higher π^* levels of 2,5-DM-DCNQI and especially DCNE (Table II), these two ligands form complexes **3** and **2** with higher energy (MLCT) transitions.

A similar pattern is observed for the M(CO)$_5$ complexes **7**–**10**, where the system **8** with the less oxidizable tungsten fragment and the smaller (=better π interacting) TCNE ligand displays the highest (MLCT) transition energy, though it still lies in the near-infrared region of the spectrum. A comparison between optical transition energy maxima (in eV) and redox potential differences (in V)[28b,50] has to take into account the irreversible nature of the oxidation processes in all cases studied (Table II). Nevertheless, application of the approximation given by eq 8, in

$$E_{CT}\ (\mathrm{eV}) = \Delta E_{ox/red}\ (\mathrm{V}) + \chi \qquad (8)$$

which χ represents the sum of intra- and intermolecular vibrations including solvent reorganization, confirms qualitatively that the system **7** with the lowest absorption maximum among TCNE complexes also exhibits the smallest electrochemical potential difference.

Chart V



Since Cr(CO)$_2$(C$_6$Me$_6$) is a better donor than Mn(CO)$_2$(C$_5$R$_5$) fragments according to redox potentials of phosphite complexes,[24,37] complex **6** should exhibit even more LMCT character (C in Chart III) than **1** or **5**. According to representation C in Chart III the long-wavelength absorption band is shifted hypsochromically relative to that of **1** (Table III, Figure 6); however, there is now a second intense band lying rather close in the visible region. This second band is also prominent in the spectrum of **1** (Figure 3), albeit at higher energies; most remarkably, these "second" absorption bands show a *positive* solvatochromism,[29] i.e. a bathochromic shift with increasing solvent polarity (Figure 6). This unusual[31b] phenomenon indicates[29] that the excited state attained via this second transition is more polar than the ground state; we therefore describe this transition tentatively as

$$(\mathrm{R}_n\mathrm{M}^+)(\mathrm{L}^-) \xrightarrow[\text{MLCT}]{h\nu} {}^*[(\mathrm{R}_n\mathrm{M}^{2+})(\mathrm{L}^{2-})] \qquad (9)$$

The lower energy of that second transition in the case of complex **6** with its stronger electron-donating Cr(CO)$_2$(C$_6$Me$_6$) fragment is clearly compatible with eq 9 as is the absence of such a band in the long-wavelength region for complexes **2**–**4**, which show more contribution from resonance structure A in eq 1. This band can also be formulated as resulting from a coordination-affected intraligand (IL) transition of the anion radical; free TCNE$^{\bullet-}$ has a structured long-wavelength band ($\pi \rightarrow \pi^*$) with an absorption maximum at 23 375 cm^{-1} (ϵ = 8425 M^{-1} cm^{-1}) in acetonitrile or dichloromethane.[9c] In both descriptions the LUMO of TCNE is doubly occupied upon excitation, the difference is whether the electron is promoted from a metal- or ligand-based orbital or from a mixture thereof.

Ordinarily, an MLCT transition produces a negatively solvatochromic response because—in a first approximation—the charge polarization produced by the ligand-to-metal coordinative bond is reduced by the metal-to-ligand charge transfer in the excited state.[31a,b] Negative solvatochromism is also observed for the first (LMCT) bands of compounds **1** and **6** because the simplified description (eq 10) of those transitions involves a reduction of

$$(\mathrm{R}_n\mathrm{M}^+)(\mathrm{L}^-) \xrightarrow[\text{LMCT}]{h\nu} {}^*[(\mathrm{R}_n\mathrm{M})(\mathrm{L})] \qquad (10)$$

molecular polarity in the excited state. This change of polarity and the resulting solvatochromic response are particularly large for complex **6** with its more ionic (B and C in eq 1) ground state; difficulties in dissolving **6** in nonpolar media such as toluene despite the presence of a hexamethylbenzene ligand support such a view. For **1** the observed solvatochromism is not much different from that of other (L)Mn(CO)$_2$(C$_5$R$_5$) complexes with clear MLCT features:[34,51] it is thus not possible to distinguish between MLCT (A in Chart III) and LMCT (C in Chart III) on the basis of solvatochromism alone; each case has to be considered individually.[31b] Incidentally, eq 9 describes the reverse of the usual formulation for an MLCT transition;[28,52] complexes like **1** or **6** may thus be considered as models of "normal" MLCT excited states.

The solvent parameter E^*_{MLCT} derived[30a] and used[30,31] for MLCT transitions of σ-coordinated complexes can thus be employed as well for transitions of predominant LMCT character. However, this solvent parameter as well as the E_T scale clearly fail to correlate with absorption band maxima of π complexes such as **2** and **7**–**10** as illustrated by poor correlation coefficients in Table IV and by the scatter of pertinent points in Figures 6 and 7. Most indicative are three discrepancies: π complexes exhibit invariably lower absorption maxima (i) in benzene than in the less "polar" (smaller E_T[29]) but better π-donating toluene (or even mesitylene), (ii) in 1,2-dichloroethane, benzonitrile, or nitrobenzene

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(49) The importance of electron densities at the coordinating centers in determining spectral and chemical properties of "charge-transfer complexes" has been emphasized before: (a) Ernst, S.; Kaim, W. *J. Am. Chem. Soc.* **1986**, *108*, 3578. (b) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146.

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than in the less "polar" but better σ-donating tetrahydrofuran, and (iii) in acetonitrile than in the less "polar" but better σ- and π-donating acetone (Figures 6 and 7).

These results, especially point i, suggest a π type donor interaction (Chart V) between solvent molecules and a complex such as (TCNE)M(CO)$_5$ ("π solvates"); conventional donor numbers (DN) derived from complexes $Cl_5Sb{\cdot}S$ (S = solvent)[29,53] make only allowance for σ type interactions and do not seem to be applicable here (Table III).

A solvent parameter scale for π type interactions remains to be constructed;[54] such information should be valuable to all organometallic chemistry (including catalysis[1]) that makes use of π-coordinating ligands.

While no band structure was observed for the long-wavelength charge-transfer band of **7**, the tungsten analogue **8** displays a high-energy shoulder and a low-energy separate band in solvents of very low polarity (Figure 4). In agreement with previous arguments[30b–d,34,40] we assign these additional features to differently polarized transitions from the three split levels in a low-spin d^6 system; expectedly, this splitting is much smaller for Cr than for the heavier homologue W. The larger and perhaps less symmetrically coordinated[25] TCNQ π complexes **9** and **10** exhibit band structure in all solvents (Figure 5), which may in part be attributed to the presence of an IL transition of the TCNQ anion radical (ν = 11 880 cm^{-1}).[55] Infrared spectra of such solutions do not show significant amounts of dissociated TCNQ or M(CO)$_5$ solvent adducts;[25] there is, however, slow formation of $TCNQ^{\bullet-}$ in acetonitrile with its high dielectric constant[29] (cf. eq 5).

Summary. This work illustrates the intriguing variability of geometrical (σ and π coordination) and electronic structures for complexes of polynitrile acceptor ligands with transition-metal carbonyl fragments. The compounds discussed show a continuous change from systems with MLCT to those with LMCT character of the major long-wavelength transitions, depending on the back-bonding capability of coordinated d^6 metal fragments.[56] Electrochemistry, reactivity, and ESR and vibrational (ν_{CN}, ν_{CO}, ν_{CC}) as well as charge-transfer spectroscopy indicate the considerably but not completely[8] reduced nature of ligands such as TCNE or TCNQ and the weak covalent bonding in such complexes. The equally important chemical consequences of this situation, viz., the enhanced nucleophilicity of the tetradentate ligands, has only begun to be exploited, e.g. in the formation of novel tetranuclear complexes with remarkable properties.[14,57]

Acknowledgment. Support for this work has come from Deutsche Forschungsgemeinschaft, Stiftung Volkswagenwerk, Flughafen Frankfurt/Main AG, Hermann-Willkomm-Stiftung, and BASF AG. We are grateful to Professor K. Wieghardt and Dr. K. Pohl (Bochum, FRG) for near-IR measurements and to Professor S. Hünig (Würzburg, FRG) for a gift of 2,5-DM-DCNQI.

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Bonding in Transition-Metal Clusters

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Received January 27, 1989

In this paper, the application of Stone's tensor surface harmonic (TSH) theory to the bonding in transition-metal clusters is reviewed and developed by using specific examples and comparisons with previous studies. The relationship between TSH theory and the isolobal principle is described with the aid of Fenske–Hall calculations on some small transition-metal clusters. A detailed analysis of the results for $Ru_5(CO)_{15}^{2-}$ shows that the sets of orbitals expected from TSH theory are all clearly identifiable. The application of the method to nonconical cluster vertices, clusters with interstitial atoms, and some interesting metallaboranes is also discussed. Clusters with a vertex lying on an idealized principal rotation axis are particularly interesting; their electron counts and the effects of low symmetry are considered.

Introduction

The problem of understanding the electron counts in both main-group and transition metal clusters has been investigated extensively for many years. The debor principle, which emerged in the early 1970s from the work of Williams,[1] Wade,[2] and Rudolph,[3] first systemized the correlation between structure and electron counts for closo, nido, and arachno boranes. The isolobal principle, which allows transition-metal clusters to be understood in terms of the simpler borane structures, has also proved very useful.[4] The term polyhedral skeletal electron pair theory was later introduced to cover the correlation between electron count and cluster structure.[5] Its development has often been facilitated by means of extended Hückel calculations.[6] More recently Stone's tensor surface harmonic (TSH) theory[7] has been used to provide a firmer theoretical foundation for these generalizations.[8,9]

In the TSH model, approximate linear combinations of atomic orbitals are formed by using the eigenfunctions for the particle on a sphere problem (the spherical harmonics) and the tensor surface harmonics. By analogy with the relation between the Hückel wave functions for cyclic polyenes and the eigenfunctions

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